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RH(II) - CU(II) CATALYZED OXIDATION OF 1-HEXENE BY O<sub>2</sub> USING IMMO-ETC(U)

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Rh(I)-Cu(II) Catalyzed Oxidation of  
1-hexene by O<sub>2</sub> using Immobilized, Site-Separated  
Organosulfide Complexes.

by

Eric D. Nyberg and Russell S. Drago\*

School of Chemical Sciences

University of Illinois

Urbana, IL 61801

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ABSTRACT

→ Silica gel bound organosulfide ((SG)-SH) was reacted with Rh(CO)<sub>2</sub>S'<sub>n</sub>BF<sub>4</sub> (I) (S' ≡ Solvent) to produce <sup>mol</sup> (SG-S)<sub>2</sub>Rh<sub>2</sub>(CO)<sub>4</sub> (II) or (SG)-SRh(CO)<sub>2</sub>S'<sub>n</sub> (III). III was obtained from (SG)-SH sample possessing site-separated organosulfide groups, while II required proximate sulfide groups. III is the first example of a monomeric organosulfide transition metal carbonyl complex which is stable in the absence of additional, non-carbonyl ligands. Both the Rh(I) and Cu(II) species previously reported to be necessary for the O<sub>2</sub> oxidation of 1-hexene to 2-hexanone were bound to the (SG)-SH support, and found to be an effective catalytic system for this reaction. The monomeric III was much more active than the dimeric II. Increased lifetimes were observed for the (SG)-SH bound catalysts, relative to homogeneous analogues.

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Rh(I) - Cu(II) Catalyzed Oxidation of 1-hexene by  
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Eric D. Nyberg and Russell S. Drago

School of Chemical Sciences

University of Illinois

Urbana, IL 61801

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A new class of catalytic oxidations involving metal centered oxygen atom transfer to terminal olefins from dioxygen has been discovered in the past seven years.<sup>1</sup> Most recently Mimoun has reported a homogeneous system involving Rh(I), Cu(I) or Cu(II), and H<sup>+</sup> as co-catalysts for the O<sub>2</sub> oxidation of terminal olefins to methyl ketones with >98% specificity and unusually high turnovers (110 in 4hrs).<sup>1a</sup> Several workers have proposed the sequential coordination of O<sub>2</sub> and terminal olefin, followed by the formation of a five-membered peroxymetalloccycle,<sup>1a-c,2</sup> as the first steps in their oxidation reaction mechanisms. The relatively short lifetimes of the homogeneous catalysts active in this class of oxidations encouraged us to seek a functionalized solid support to site isolate the rhodium complexes, on the assumption that the catalyst deactivation process was multi-ordered in rhodium. The presumed need to

coordinate both  $O_2$  and olefin to rhodium led us to consider the use of immobilized monodentate<sup>3</sup>, anionic<sup>4</sup> ligands which would be stable to oxidation<sup>5</sup> and form strong bonds with Group VIII transition metals. We report here 1) the preparation of novel monomeric organosulfide-rhodium carbonyl complexes which do not have a counterpart in solution chemistry, and 2) the effectiveness of the organosulfide supported Rh(I) - Cu(II) system in the catalytic oxidation of 1-hexene to 2-hexanone using dioxygen.

A series of silica gel bound organosulfide samples ( $\textcircled{\text{SG}}\text{-SH}$ ) were produced varying only in their sulfide concentrations (0.20, 0.10, 0.050 and 0.025 mmole  $S/g \textcircled{\text{SG}}$ ) by reacting Davison Grade 62 silica gel with  $(CH_3O)_3Si(CH_2CH_2CH_2SH)$  in refluxing xylenes. These were reacted with freshly prepared  $Rh(CO)_2S'_nBF_4$  ( $S' \equiv$  solvent) (I) in THF<sup>6</sup> or EtOH under Ar, producing orange to lemon-yellow  $\textcircled{\text{SG}}\text{-SH}$  supported rhodium complexes. Infrared spectra in the CO region for the supported rhodium complexes were recorded after bubbling CO through EtOH suspensions at RT for several hours.<sup>7</sup> The three band spectrum<sup>8</sup> for the  $\textcircled{\text{SG}}\text{-SH}$  bound (I) using the 0.20 mmole  $S/g \textcircled{\text{SG}}$  support clearly identified the supported species as the dimer  $(\mu\text{-}\textcircled{\text{SG}}\text{-S})_2Rh_2(CO)_4$  (II).<sup>9</sup> This is produced from proximate silica gel bound sulfide groups. In contrast, the supported rhodium complex produced from (I) and the 0.050 mmole  $S/g \textcircled{\text{SG}}$  support was characterized as  $\textcircled{\text{SG}}\text{-SRh(CO)}_2S'_n$  (III) from its two band infrared spectrum.<sup>10</sup> The supported rhodium complex formed using the 0.10 mmole  $S/g \textcircled{\text{SG}}$  support was shown by infrared to consist of a mixture of both the monomeric and dimeric rhodium carbonyl complexes. To our knowledge (III) is the first example of a monomeric organosul-

fide transition metal carbonyl complex which is stable in the absence of additional non-carbonyl ligands. A number of monomeric organosulfide carbonyl transition metal complexes have been reported,<sup>11</sup> but all require stabilizing ligands such as cyclopentadiene or phosphines, or strong electron withdrawing groups (such as  $F_3CS^-$  or  $F_5C_6S^-$ ) on the organosulfide. In the absence of these features any monomeric metal sulfides that may be formed in solution quickly react to form the dimers and lose CO. The replacement of CO with more inert ligands or the use of the much weaker fluorinated sulfide base may inhibit this process. The physical site isolation of the organosulfide ligands obtained with the 0.050 mmole S/g (SG) support enables the formation of the coordinatively unsaturated (III) in the absence of either special ligands or weak base sulfides. (III) can be heated overnight at 70.°C in the presence of all oxidation reaction components (vide infra) except O<sub>2</sub>, and reformed by exposure to CO. The loss of CO is quite facile in the presence of O<sub>2</sub>, but reversible.

The Rh(I), Cu(II), H<sup>+</sup> catalyzed oxidation of 1-hexene to 2-hexanone was carried out using the series of (SG)-SH supported rhodium species characterized above. The results are presented in Figure 1. It is apparent from this data that as the silica gel's surface sulfide concentration is decreased the catalyst activity increases. Thus it appears that the active catalyst precursor is the monomer (III), while the dimer (II) forms a much less active, or inactive, catalyst. The homogeneous system (no (SG)-SH added) in the presence of slightly more than two equivalents of (CH<sub>3</sub>O)<sub>3</sub>-Si(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH) was almost completely inactive. The rhodium catalyst precursor formed in this solution is [Rh(CO)<sub>2</sub>(RS)]<sub>2</sub>, and

is analogous to the supported rhodium dimer (II). The homogeneous system in the absence of silane exhibited an induction period of 40 min, then catalyzed the oxidation at a very fast rate (the profile for this system can be seen in Figure 2). After 24hrs however, its activity had dropped to only 0.9% of the initial rate. In contrast, the activity of an analogous catalytic oxidation using (III) (with 0.025 mmole S/g (SG); curve B in Figure 1) after 24hrs of reaction was 7.4% its initial rate. As a result the supported system (III) was actually twice as active as the homogeneous solution at 24hrs. The most striking feature in Figure 1 is the complete inhibition of catalyst degradation after 7hrs using (III) with  $\text{HClO}_4$  as the proton source (curve A). In this case the rate of 1-hexene oxidation is a constant 0.70 turnovers/hr over the final 17hrs of reaction (19% of the initial rate). This is in marked contrast to the result obtained with the homogeneous system in which catalyst deactivation is rapid and dominant. The large improvement in the supported catalyst stability using  $\text{HClO}_4$  rather than  $\text{H}_2\text{SO}_4$  (curve B) is likely the result of the poorer ligating ability of  $\text{ClO}_4^-$  relative to  $\text{SO}_4^{2-}$ . This would prevent the leaching of rhodium due to the proton's counter-ion coordination, and the catalyst's subsequent oxidative and/or aggregative deactivation.

Enough (SG)-SH must be added to bind all Rh(I) and Cu(II) or extensive rhodium leaching into solution results from the competition by Cu(II) for sulfide groups. To further establish that the oxidation was catalyzed by the (SG)-SH bound rhodium complex, and not leached rhodium, the filtrate was syringed off under reaction conditions (50 psi  $\text{O}_2$ , 70. $^\circ\text{C}$ ), 0.074 mmole Cu(II) added, and the reaction re-started to check for catalytic activity. For the 0.050

mmole S/g (SG) sample leached rhodium accounted for only 14% of the total activity at 3.5 hrs, which considering the much greater initial activity of homogeneous (I) suggests that only 5% of the active rhodium complex was present in the solution under the reaction conditions. On mixing together the reaction components at RT using any sample of (SG)-SH all Rh(I) and Cu(II) were bound to the support. The supported complex (III) (using 0.050 mmole S/g (SG)) and homogeneous (I) (in the absence of silane) were also used for the oxidation of 1-hexene at 90.°C using H<sub>2</sub>SO<sub>4</sub> as the proton source. As seen in Figure 2 the supported catalyst is even more resistant to deactivation at 90.°C than it was at 70.°C when compared to the homogeneous system.

The inactivity of homogeneous organosulfide complexes in catalysis (outside of electron transfer roles) is a direct result of sulfide's strong bridging ability which effectively eliminates necessary coordination sites. The demonstration of 1) the stability of the monomeric organosulfide rhodium carbonyl complexes reported here (with respect to dimerization) in cases of effective site isolation on silica gel, 2) the ability of the (SG)-SH supported Rh(I)-Cu(II) system to effectively catalyze the oxidation of 1-hexene, and 3) the inhibition of catalyst decomposition by site isolation of Rh(I), serve as yet another example of the unique role which may be served by functionalized polymers as supports for transition metal complexes.<sup>12</sup> The greater resistance to catalyst deactivation with the site isolated monomeric (III) compared to either the dimer (II) or the homogeneous (I) may be a result of a stabilizing influence of the sulfide ligand to irreversible monomeric rhodium oxidation, and/or the effectiveness of rhodium site isolation in inhibiting multi-ordered decomposition mechanisms. We are currently investigating the role of Cu(II) in



this system by further diluting the silica gel surface in organo-sulfide to achieve site-separation of Rh(I) and Cu(II). The most dilute samples reported here (0.025 mmole S/g (SG)) most likely allow some Rh(I) - Cu(II) interaction. A drop in supported catalyst activity with further dilution would implicate the need for the direct interaction of Rh(I) and Cu(II) in the reaction mechanism.

#### Acknowledgments

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4. Mimoun reported, and we have further investigated, the role of chloride in improving the catalyst lifetimes. The homogeneous system's activity (used for comparison in this report) may be improved to 193 turnovers in 24hrs simply by adding three equivalents of chloride. The reaction in this case proceeded identically to that when using Mimoun's precursors:  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . We feel this is a result of chloride coordination inhibiting rhodium complex aggregation. Indeed, this effect is maximized at five equivalents of chloride, resulting in 343 turnovers in 24hrs, with all the improvement coming from much slower catalyst de-activation (the initial rates with 3 and 5 equivalents  $\text{Cl}^-$  were identical).
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Figure 1

All reactions were run at 70.°C under 52 psi O<sub>2</sub> after mixing components at RT. Used for each run were 0.074 mmole Rh(CO)<sub>2</sub>S<sub>n</sub>BF<sub>4</sub> (as a freshly prepared EtOH solution), 0.16 mmole S (as (SG)-SH), 0.074 mmole Cu(NO<sub>3</sub>)<sub>2</sub>·2½H<sub>2</sub>O, 0.148 mmole H<sub>2</sub>SO<sub>4</sub> or 0.222 mmole HClO<sub>4</sub> (see below), 0.568 mmole 2-heptanone (as an internal standard), 45 ml EtOH (distilled over CaCO<sub>3</sub>), and 15.0 ml 1-hexene (distilled over CaH<sub>2</sub>, passed through alumina). Curve A: used 0.222 mmole HClO<sub>4</sub> as the proton source; 0.025 mmole S/g(SG) as the support. Curve B: 0.148 mmole H<sub>2</sub>SO<sub>4</sub> as the proton source; 0.025 mmole S/g(SG). Curve C: 0.148 mmole H<sub>2</sub>SO<sub>4</sub>; 0.050 mmole S/g(SG). Curve D: 0.148 mmole H<sub>2</sub>SO<sub>4</sub>; 0.10 mmole S/g(SG). Curve E: 0.148 mmole H<sub>2</sub>SO<sub>4</sub>; 0.20 mmole S/g(SG). 2-hexanone production was monitored using GLC, with 2-heptanone as an internal standard.

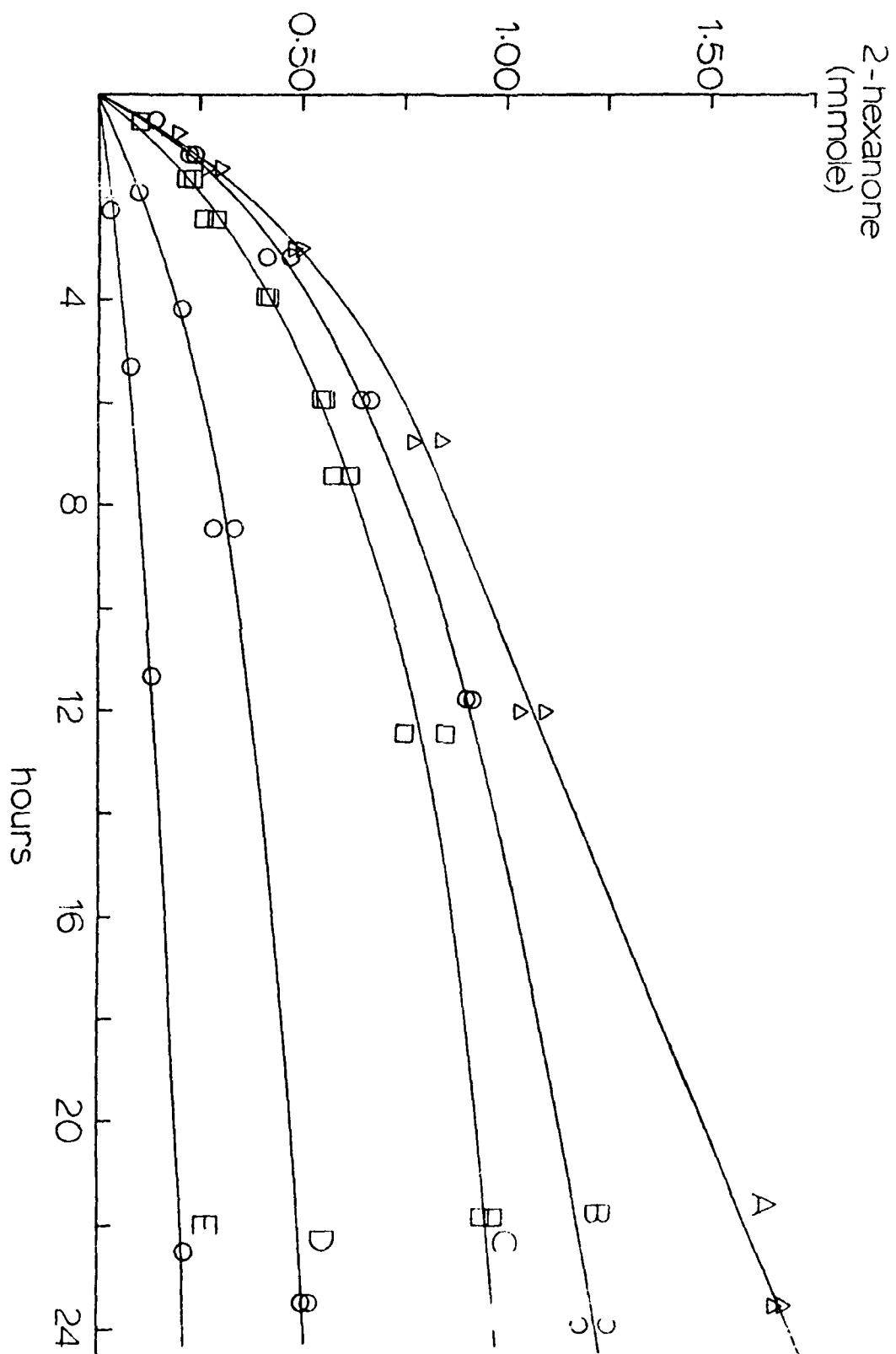


Figure 2

All reaction systems were prepared as in Figure 1, at 70.°C or 90.°C as indicated near each curve. ( $\Delta$ ) are homogeneous systems (no (SG)-SH added). (c) are (SG)-SH supported systems, using 0.050 mmole S/g(SG)

